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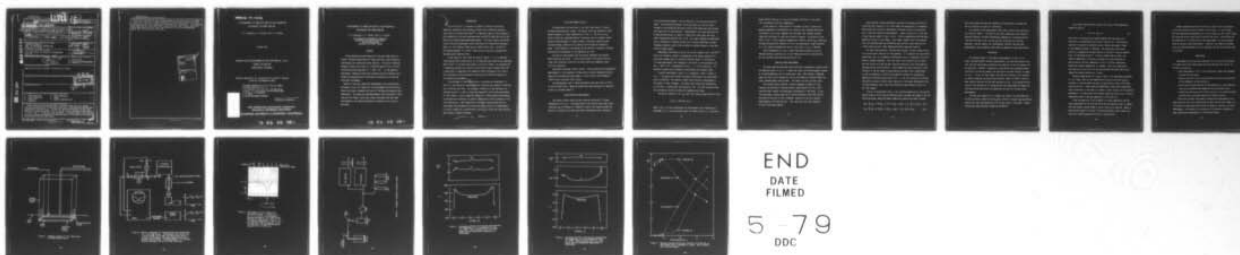
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CO MEASUREMENTS IN COMBUSTION GASES BY LASER ABSORPTION SPECTRO--ETC(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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**CO MEASUREMENTS IN COMBUSTION GASES BY LASER ABSORPTION
SPECTROSCOPY AND PROBE SAMPLING**

S. M. Schoenung, R. K. Hanson, and P. K. Falcone

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CO MEASUREMENTS IN COMBUSTION GASES BY LASER ABSORPTION
SPECTROSCOPY AND PROBE SAMPLING

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ABSTRACT

Carbon monoxide has been measured in the post-flame region of laminar, premixed hydrocarbon/air flames using both laser absorption spectroscopy and conventional probe sampling. The optical technique employed a diode laser tuned to a vibration-rotation line in the CO infrared absorption spectrum at $\nu = 2077.1 \text{ cm}^{-1}$. In the sampling experiments, combustion gases were extracted using an uncooled, aerodynamically-quenched quartz microprobe and analyzed for CO and CO₂ using NDIR instruments.

Results of the laser absorption measurements of CO concentration performed in fuel-rich flames are in good agreement with equilibrium predictions based on metered fuel and air flowrates and measured local temperature. The sampling probe measurements, which were made in both lean and rich flames, yield total carbon consistent with the input stoichiometry, but indicate substantial conversion of CO to CO₂ in the probe.

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INTRODUCTION

The initial work in a program at Stanford to develop laser-based combustion diagnostics has focused on tunable laser absorption spectroscopy using an infrared diode laser. An important aspect of this program is the validation of the laser technique under controlled conditions and by comparison with established probe-based methods. This paper reports preliminary results from such experiments, which consisted of CO concentration measurements in a flat premixed flame using a tunable diode laser, and both CO and CO₂ measurements in a similar flame using an uncooled, aerodynamically quenched quartz sampling probe.

CO was chosen for this study for several reasons: it is an important flame species whose concentration can be predicted under equilibrium conditions which prevail in the post-flame region of fuel-rich flames; its concentration in combustion products can be easily varied from 10 ppm to greater than 10%, a range which is compatible with commercial NDIR instruments; and it has a well-understood infrared absorption spectrum which simplifies analysis of the absorption measurements.

The advantages of laser absorption as a technique are substantial in that it is non-intrusive, species-specific, sensitive and capable of resolving fast variations with time. The principal limitation of the technique, for some applications, is that it yields an integrated line-of-sight measurement. For this reason, it was an important objective of these sampling measurements to determine the uniformity of species concentration profiles produced in the flat flame burner. Other objectives of the sampling experiments were to investigate the performance of an uncooled quartz probe for CO measurements in various flames and, by monitoring CO and CO₂, to verify the flame stoichiometry based on metered flowrates.

FLAT-FLAME BURNER FACILITY

The experiments were performed in the post-flame region of laminar, pre-mixed hydrocarbon/air flames. The burner, which was operated at atmospheric pressure, is shown schematically in Fig. 1. The 4 cm x 10 cm burner surface was honeycomb material (stainless steel or ceramic), water-cooled around the edges; a ceramic chimney, fitted with cooled calcium fluoride windows, defined a 10 cm optical path through the combustion gases. During operation, the chimney top was partially covered to minimize recirculation disturbances to the combustion gas flow.

Fuel and air were metered with calibrated rotameters and premixed before entering the burner. A bed of glass beads in the burner base provided flow uniformity, which was verified by hot-wire anemometry under cold-flow conditions.

Experiments performed to date include: laser absorption and thermocouple measurements in rich propane/air flames using a ceramic honeycomb surface; sampling and thermocouple measurements in both rich and lean methane/air flames using a stainless steel surface.

The thermocouples used in these experiments were made from 2 or 5 mil Pt and Pt-10% Rh wires. Measured temperatures were corrected for radiation losses by a standard method.²

LASER ABSORPTION MEASUREMENTS

The optical system, which has been reported previously,¹ is shown schematically in Fig. 2. The output beam of the tunable diode laser (Laser Analytics) was collimated to a diameter of about 3 mm, passed through the burner at a location 2 cm above the ceramic honeycomb surface, through a

1/2 m grating monochromator, and was then split into two equal-intensity beams. One beam passed through a 10 cm absorption cell and the other through a solid germanium Fabry-Perot etalon; both beams were then focused onto cooled (77 K) InSb detectors. Monochromator slits were typically set at 200 and 500 microns to obtain a single axial laser mode; the laser power reaching each detector was 1-5 μ W. The laser frequency was modulated using a combined dc injection current and a variable amplitude, variable frequency sawtooth current (both provided as standard outputs of the Laser Analytics power supply).

Measurements were made by tuning the narrow-linewidth laser ($<10^{-4} \text{ cm}^{-1}$) across the frequency interval corresponding to the energy required for a transition between specific vibration-rotation states in a CO molecule. For these experiments, the frequency at the center of the absorption line was $\nu = 2077.1 \text{ cm}^{-1}$, corresponding to the $\nu = 1, P(10)$ transition. The absorption spectra were recorded on single-sweep oscilloscope traces.

A typical experimental result, for a propane/air flame, is shown in Fig. 3. The upper trace records the power transmitted by the Fabry-Perot etalon (0.0495 cm^{-1} free spectral range) which provides a measurement of the change in laser frequency. The lower trace records the transmission as the laser is tuned across the absorption line. The zero-intensity trace was recorded by blocking the beam and resweeping the scope.

The partial pressure of CO, P_{CO} (atm), was found by applying Beer's Law:

$$(I/I_0)_\nu = \exp(-S\phi_\nu P_{\text{CO}} L),$$

where I and I_0 are the transmitted and non-absorbed laser intensities at wavenumber ν , L is the pathlength across the flame (10 cm), ϕ_ν is the line-

shape function (cm) and S is the line strength ($\text{cm}^{-2}/\text{atm}$) of the transition, evaluated at the local temperature.

In the analysis, a Voigt profile is assumed in order to convert the observed absorption line halfwidth to a value for the lineshape function at line center¹; this value, together with the known line strength and path length are sufficient to infer the CO partial pressure. An analysis of the trace in Fig. 3, with a measured temperature of 1974 K, yields $P_{\text{CO}} = 0.083 \text{ atm}$. The equilibrium partial pressure of CO for the experimental flame conditions ($\phi = 1.37$, based on metered fuel and air flow rates) is $P_{\text{CO}} = 0.084 \text{ atm}$.

Future experiments will use a signal-averaging technique to provide improved accuracy, particularly in lean flames where the CO concentrations and the resulting fractional absorptions are low.

SAMPLING PROBE MEASUREMENTS

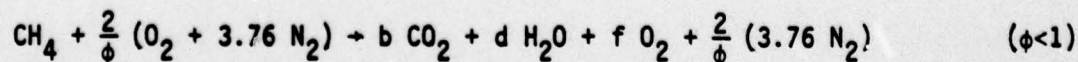
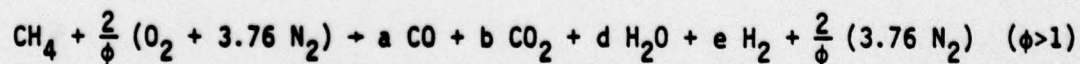
The probe sampling experiments were performed in methane/air mixtures using the apparatus shown in Fig. 4. A sample was drawn into the microprobe, through an ice bath/condensate trap to remove water vapor, then through a diaphragm pump, and finally split between CO and CO₂ non-dispersive infrared (NDIR) analyzers (Beckman Models 850 and 840). The sample line was stainless steel.

The uncooled quartz sampling probe was designed to quench $\text{CO} \rightarrow \text{CO}_2$ reactions by operating at reduced pressure (approximately 85 Torr), while causing minimal thermal and aerodynamic disturbances in the flame. To provide the sample flowrate required by the NDIR analyzers, about 600 scc/min, the probe orifice was 0.4 mm in diameter, opening to 5 mm at a location approximately 2 cm along the axis. This large area ratio was necessary to avoid frictional choking.

Data obtained in these experiments consisted of transverse profiles of CO and CO₂ mole fractions in the dried sample and temperature, all measured above the burner surface at approximately the same location as the optical axis in the laser absorption measurements. Typical profiles for a rich and a lean flame are shown in Figs. 5 and 6. The CO concentration profiles were generally uniform in rich flames. Lean flames, however, had a flat central core, but exhibited some non-uniformity near the walls, which was due to a lifted flame zone and a lower temperature which slowed the kinetics.

For each flame condition, the data were analyzed to obtain single values of CO and CO₂ mole fractions for two purposes: 1) to compare with equilibrium predictions, and 2) to compute an equivalence ratio for comparison with that based on metered flowrates. The first step in this analysis was to select the core values of CO and CO₂ mole fractions measured in the dried sample as representing the entire profiles. These numbers were then converted to mole fractions in the wet sample by approximating the water vapor concentration as that corresponding to equilibrium combustion products at the measured temperature and metered equivalence ratio. It was also necessary to consider the partial pressure of water vapor remaining in the sample downstream of the ice bath/condensate trap, since this amounted to approximately 5 mole % of the "dry" sample.

Finally, an equivalence ratio, ϕ , was inferred algebraically from the wet sample values of CO and CO₂ by balancing carbon, hydrogen and oxygen in the following reactions, where only major combustion products have been included:



This equivalence ratio was then compared with that based on metered fuel and air flowrates to check for consistency.

The results of such measurements, made under various flame conditions, are listed in Table I. Included are the input equivalence ratio based on metered flowrates, corrected thermocouple temperature, calculated equilibrium mole fractions of CO, CO₂ and H₂O, mole fractions of CO and CO₂ measured in the wet sample, the stoichiometry inferred from the probe measurements, and an apparent probe freezing temperature (described below).

DISCUSSION

An important result of the sampling measurements is that, in all cases, the data analysis recovers approximately the input equivalence ratio. This verifies the accurate calibration and operation of the flow meters and gas analyzers. However, a comparison of the equilibrium and measured mole fractions of CO and CO₂ reveals two significant non-ideal effects, as shown in Fig. 7. First, for lean flames, the high mole fractions of CO indicate an expected chemical non-equilibrium condition, where CO formed in the primary reaction zone has not yet been converted to CO₂. This non-equilibrium rules out the possibility of validating the laser measurement by comparison with equilibrium predictions and emphasizes the need for reliable probe measurements.

The data also suggest for all flames, and notably rich ones where the CO mole fraction is lower and the CO₂ mole fraction is higher than equilibrium predictions, that some conversion of CO to CO₂ occurs in the probe. Similar effects have been observed by Kramlich and Malte.³

The primary reaction which converts CO to CO₂ in high-temperature combustion gases is



This reaction continues as the sample expands into the probe until conditions are reached where the rate of reaction (1) is sufficiently slow that no further CO oxidation occurs, leaving the sample "frozen" at the composition which is observed. The conditions at which the reaction is quenched can be described by an effective "freezing temperature", as discussed by Bray.⁴ In Bray's sudden-freezing model, the chemical composition of the gas is assumed to be that predicted by equilibrium at the local temperature, until a critical temperature, termed the freezing temperature, is reached. Below this temperature, the kinetics are too slow to follow the changing conditions and the gas composition remains constant or "frozen".

Freezing temperatures are listed in Table I for experiments performed in rich flames; they are the temperatures at which the CO and CO₂ mole fractions in the wet sample are equal to equilibrium values at the known equivalence ratio. These freezing temperatures, rather than representing actual conditions in the probe, are simply a useful measure of its quenching performance. An ideal probe, with perfect quenching, would give a freezing temperature equal to the gas temperature at the probe tip.

Since one objective of this program is to make comparative simultaneous measurements of CO using the laser and the sampling probe, it appears that the present uncooled probe is not as effective as desired. Hence, a water-cooled probe will be used in future experiments, which should substantially improve quenching of the CO \rightarrow CO₂ reactions.

Another consideration which has arisen in these initial experiments is the non-uniform CO profile present in lean flames. In such flames, the laser absorption measurements will be an average over the line-of-sight, and hence may differ significantly from the core value. Such effects can be accounted for in validating the laser measurement, but the assessment requires reliable probe measurements. Therefore, the comparison between laser and probe measurements will be completed when the water-cooled probe is available.

CONCLUSIONS

Measurements which have been completed thus far using the techniques of tunable diode laser spectroscopy and probe sampling have lead to the following conclusions:

- Laser measurements of CO in rich hydrocarbon flames show agreement with equilibrium values.
- Sampling data have verified the accurate calibration and operation of the rotameters and gas analyzers.
- Non-uniform CO concentrations at the boundaries of lean flames may need to be considered when comparing laser and probe results.
- Significant conversion of CO to CO₂ can occur in an uncooled quartz sampling probe, even when operated at reduced pressure.

Future work includes simultaneous concentration measurements to be made using the laser and a cooled probe in both rich and lean flames, for the purpose of evaluating the accuracy and detection limits of the laser measurement. Also planned is an extension of the optical technique to make time-resolved measurements in fluctuating flames.

ACKNOWLEDGEMENTS

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REFERENCES

1. R. K. Hanson, P. A. Kuntz, and C. H. Kruger, "High-Resolution Spectroscopy of Combustion Gases Using a Tunable IR Diode Laser," Applied Optics 16, 2045 (1977).
2. W. E. Kaskan, Sixth Symposium (International) on Combustion, p. 134, Chapman and Hall, London (1957).
3. J. C. Kramlich and P. C. Malte, "Modeling and Measurement of Sample Probe Effects on Pollutant Gases Drawn from Flame Zones," Combustion Science and Technology 18, 91 (1978).
4. K. N. C. Bray, "Atomic Recombination in a Hypersonic Wind-tunnel Nozzle," J. Fluid Mech. 6, 1 (1958).

Table I. Results of Probe Sampling Experiments in Methane/Air Flames

ϕ (metered)	Thermocouple Temperature, K (corrected)	X_{CO} , mole % (equilibrium)	X_{CO} , mole % (wet sample)	X_{CO_2} , mole % (equilibrium)	X_{CO_2} , mole % (wet sample)	ϕ (sample)	Freezing Temperature, K
1.52	1790	8.41	6.83	4.18	5.76	1.52	1285
1.38	1810	6.82	5.08	5.02	6.83	1.39	1220
1.17	1750	3.55	0.691	7.06	9.33	1.08	900
0.98	1637	0.00453	0.0588	9.29	9.33	0.98	
0.95	1609	0.00203	0.0443	9.03	9.30	0.97	
0.89	1562	0.00072	0.0158	8.55	8.88	0.92	

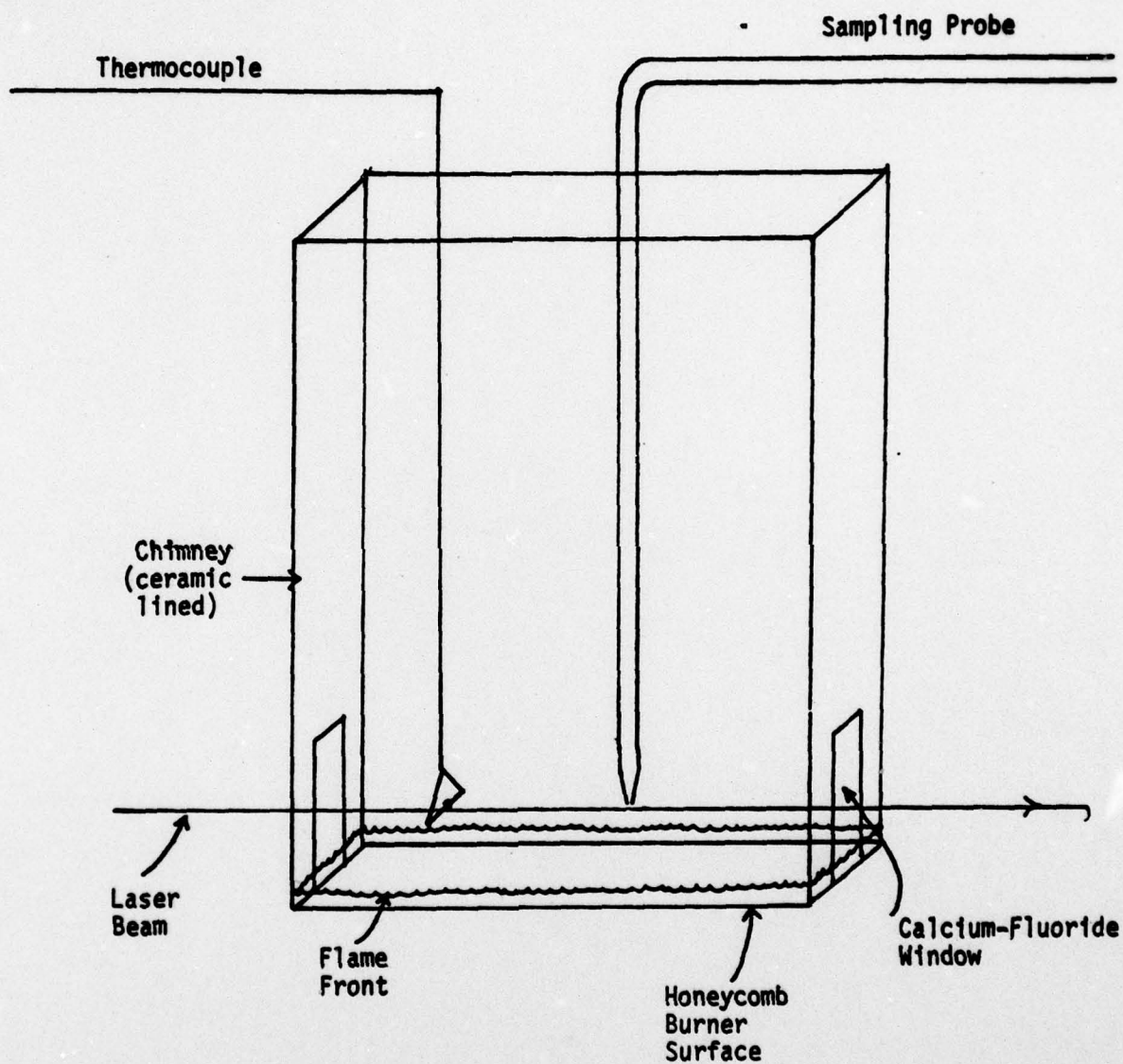


Figure 1. Schematic diagram of flat flame burner and experimental set-up.

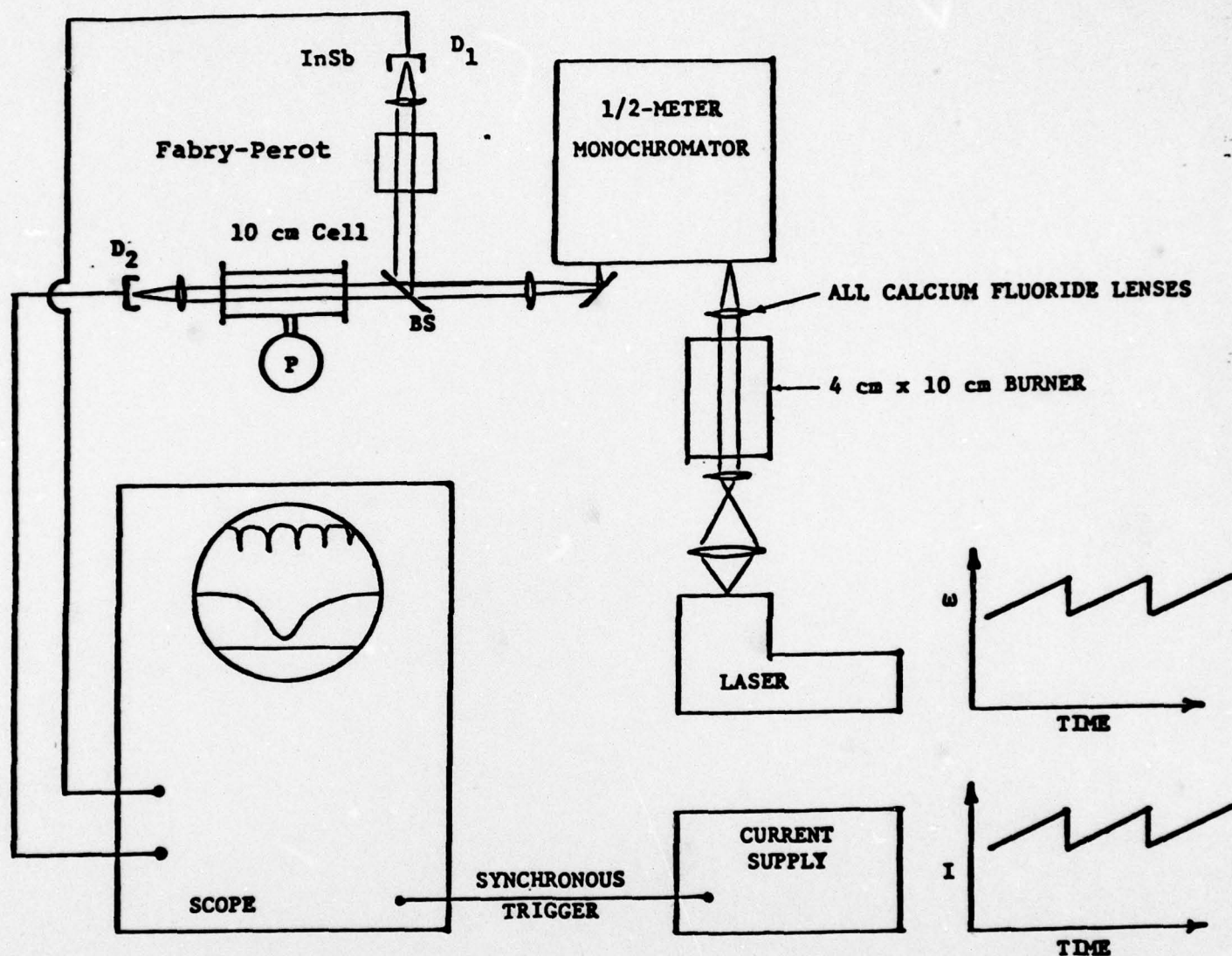


Figure 2. Optical arrangement for tunable diode laser spectroscopy in a flat flame burner. The detectors (D₁ and D₂) are liquid-nitrogen cooled InSb; the Fabry-Perot etalon is Ge (2.54 cm thickness); BS denotes beam splitter and P denotes pressure gauge. The monochromator is a 1/2-meter grating instrument (Jarrell-Ash Ebert mounting).

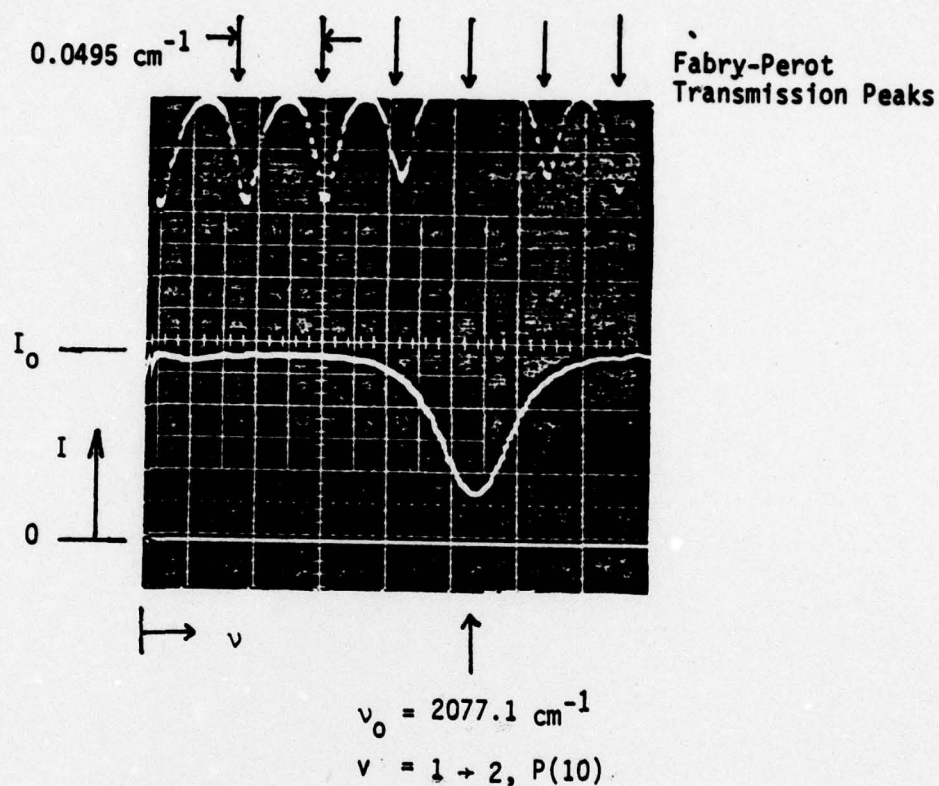


Figure 3. Oscillogram of fully resolved CO_2 absorption line at $\nu = 2077.1 \text{ cm}^{-1}$ ($\nu = 1 \rightarrow 2, P(10)$) in an atmospheric pressure propane-air flat flame burner. The fuel-air equivalence ratio is 1.37. The measured temperature is 1974 K, and the calculated partial pressure of CO is 0.083 atm. The equilibrium partial pressure of CO is 0.084 atm.

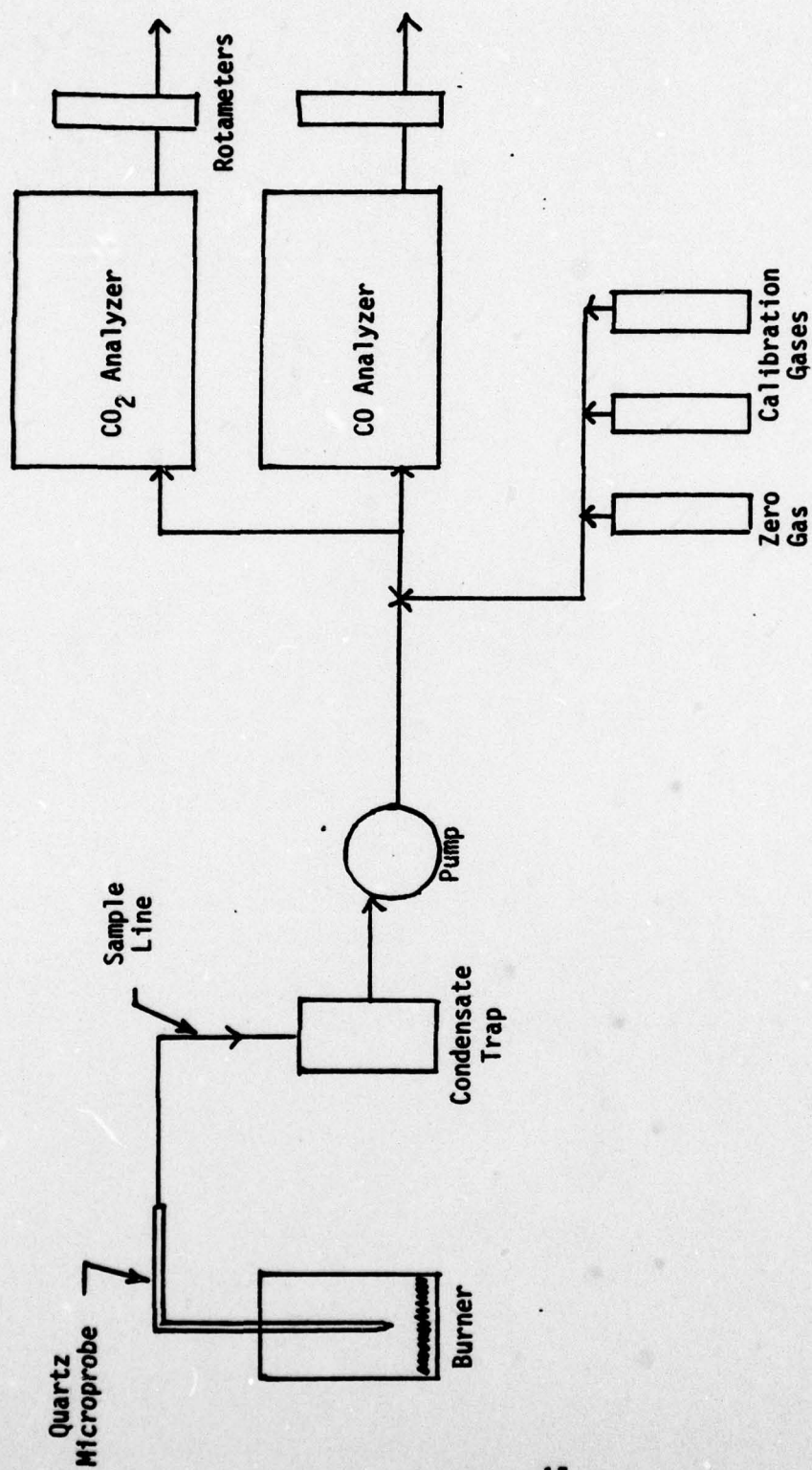


Figure 4. Schematic diagram of sampling system.

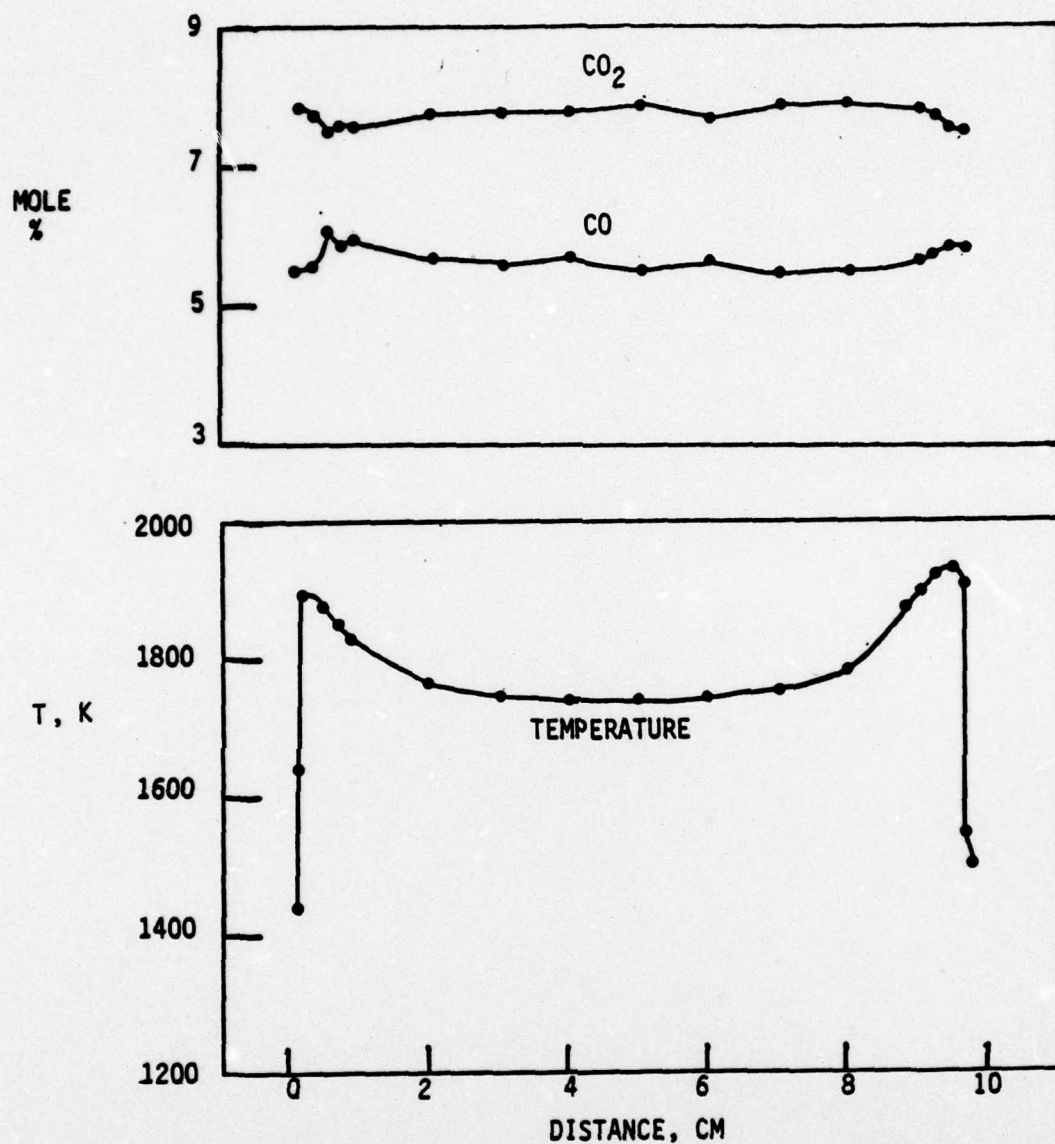


Figure 5. Transverse profiles of CO and CO_2 concentrations and temperature in a rich methane/air flame ($\phi = 1.38$). Mole fractions are in the dried sample and the thermocouple temperature is uncorrected.

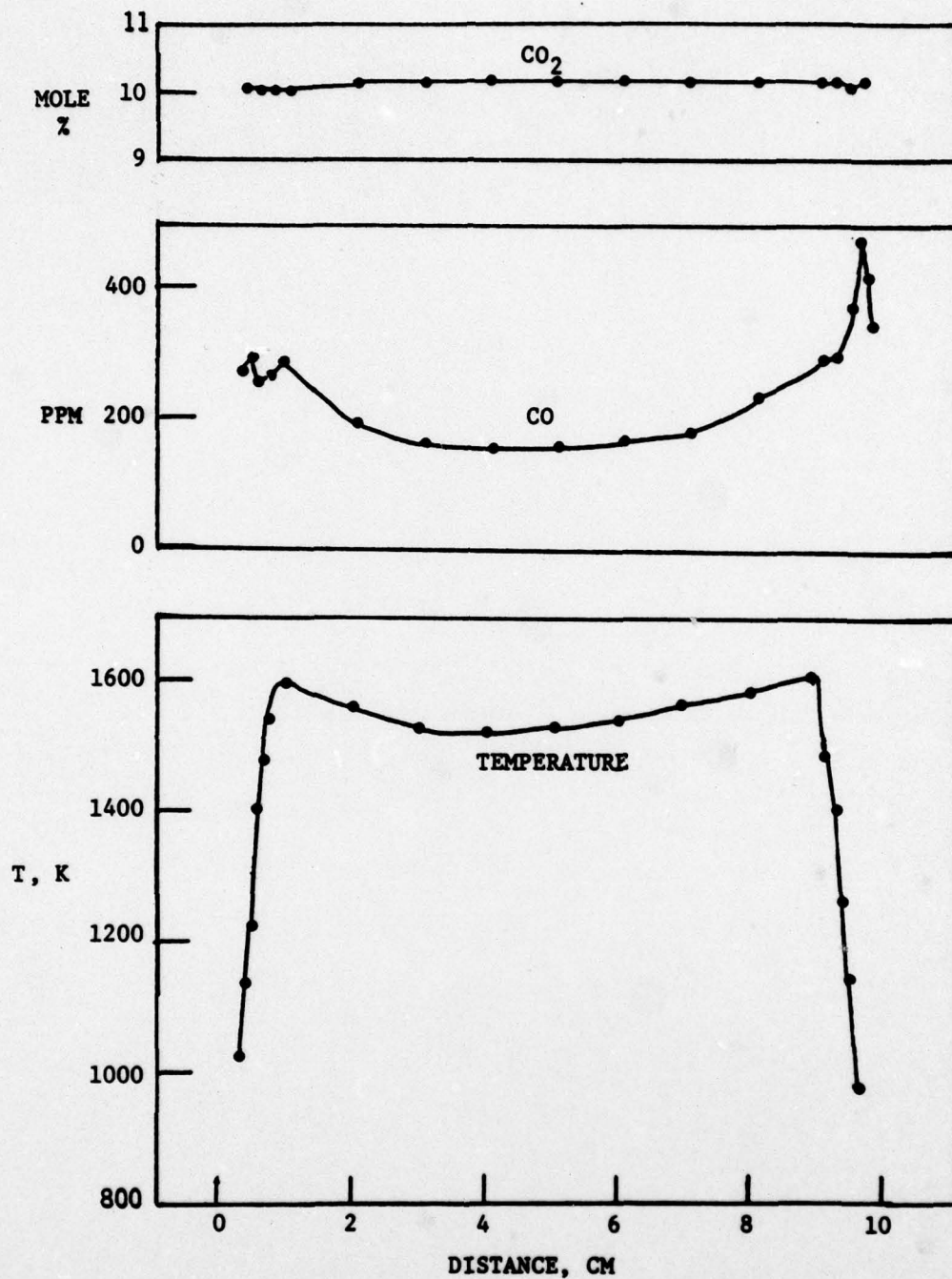


Figure 6. Transverse profiles of CO and CO_2 concentrations and temperature in a lean methane/air flame ($\phi = 0.89$). Mole fractions are in the dried sample and the thermocouple temperature is uncorrected.

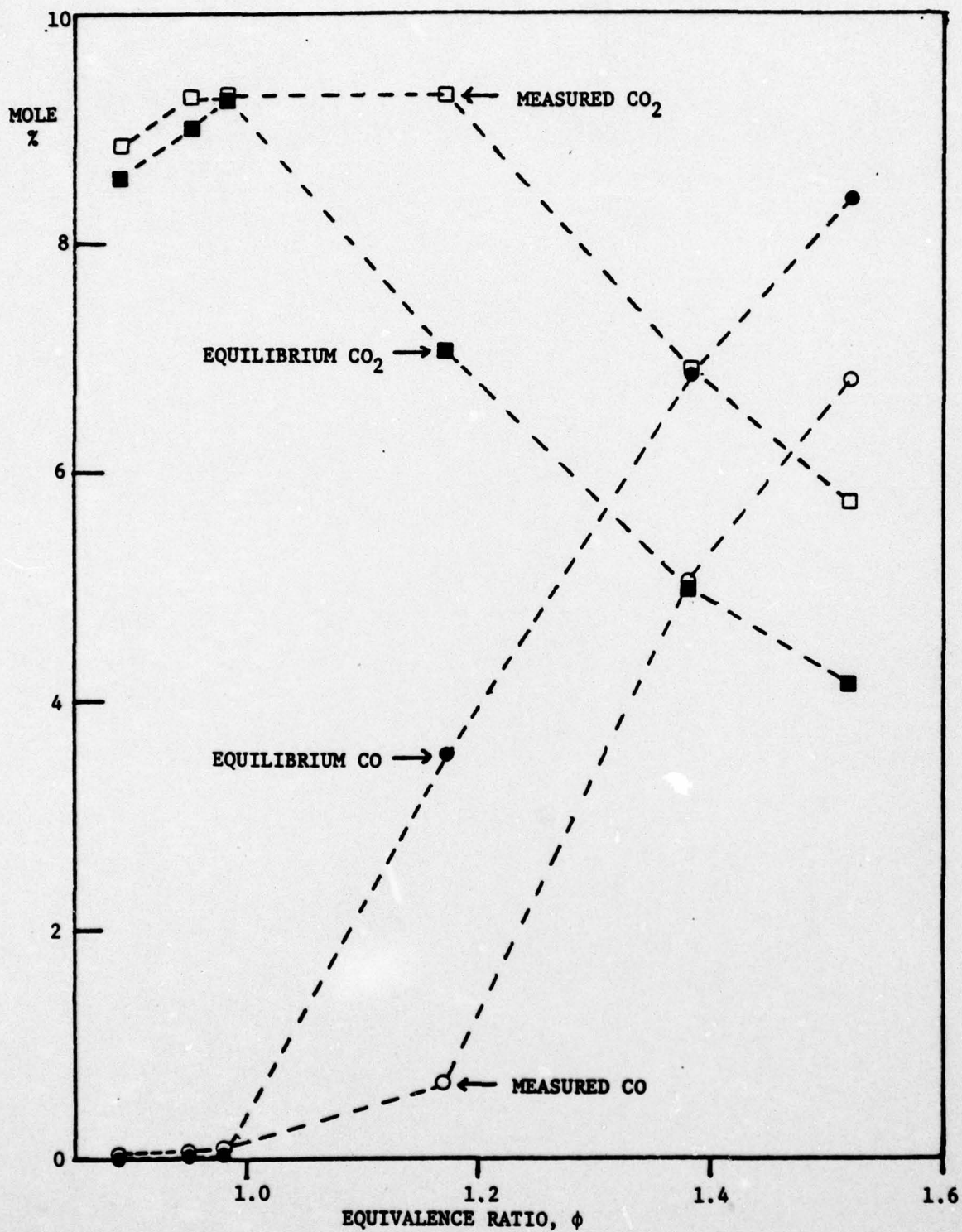


Figure 7: Measured and equilibrium mole fractions of CO and CO_2 vs. equivalence ratio in methane/air flames. Mole fractions are in the wet sample.